Lecture #5: How to read a band diagram, methods to calculate band structure

→ How to read a band diagram: Presentation Crystal Structures Energy Bands.odp

Calculating band structure

Wannier states

Consider the identities: $\begin{cases} \delta_{\vec{k},\vec{k}'} = \frac{1}{N}\sum_{\vec{R}} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}} = \sum_{\vec{R}} \underbrace{\langle \vec{k}' | \vec{R}\rangle}_{e^{-i\vec{k}'\cdot\vec{R}}} \underbrace{\langle \vec{R} | \vec{k}\rangle}_{e^{i\vec{k}\cdot\vec{R}}} \Rightarrow \langle \vec{R}|\vec{k}\rangle \perp \vec{R} \\ \delta_{\vec{R},\vec{R}'} = \frac{1}{N}\sum_{\vec{k}\in BZ} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \end{cases}$

"$\langle \vec{R}|\vec{k}\rangle$ is a "complete set". (Spans the Hilbert space)

These lead to another way to expand Bloch states:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{R}} \underbrace{\phi_n(\vec{R},\vec{r})}_{\text{Wannier state, a "localized" state}} e^{i\vec{k}\cdot\vec{R}} \quad \text{, with inverse relation}$$

$$\phi_n(\vec{R},\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}\in BZ} \psi_{n\vec{k}}(\vec{r})\, e^{-i\vec{k}\cdot\vec{R}}.$$

$$= \frac{1}{\sqrt{NV}}\sum_{\vec{k}} \underbrace{u_{n\vec{k}}(\vec{r}-\vec{R})}_{\text{only depends on } (\vec{r}-\vec{R})!} e^{i\vec{k}\cdot(\vec{r}-\vec{R})} \equiv \phi_n(\vec{r}-\vec{R})$$

$$\Rightarrow \psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{R}} \phi_n(\vec{r}-\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

▶ Bloch state can be written as a sum of localized states, each centered at a different cell in the lattice.

To a first approximation the Wannier states should look like atomic orbitals centered at each atom; However, we can prove that they are orthogonal:

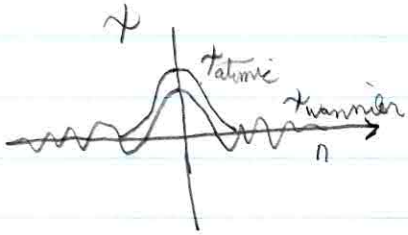
$$\langle \phi_n(\vec{R}) | \phi_{n'}(\vec{R}') \rangle = \int d^3r \frac{1}{\sqrt{N}} \sum_{\vec{k}} \psi^*_{n\vec{k}}(\vec{r}) e^{-i\vec{k}\cdot\vec{R}} \frac{1}{\sqrt{N}} \sum_{\vec{k}'} \psi_{n'\vec{k}'}(\vec{r}) e^{-i\vec{k}'\cdot\vec{R}'}$$

$$= \frac{1}{N} \sum_{\vec{k},\vec{k}'} e^{i(\vec{k}\cdot\vec{R} - \vec{k}'\cdot\vec{R}')} \underbrace{\int d^3r \, \psi^*_{n\vec{k}}(\vec{r}) \psi_{n'\vec{k}'}(\vec{r})}_{= \delta_{n,n'} \delta_{\vec{k},\vec{k}'}}$$

$$= \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} = \delta_{\vec{R},\vec{R}'} \quad //$$

$\Rightarrow$ This is quite different from atomic orbitals, since the latter overlap for different atoms

$\Rightarrow$ Wannier states are oscillating at their tail



Wannier states are <u>not</u> energy eigenstates. But they can be used to compute the band structure:

<u>Tight binding approximation</u>

From

$$\mathcal{H}|\psi_{n\vec{k}}\rangle = E_{n\vec{k}}|\psi_{n\vec{k}}\rangle$$

$$(\mathcal{H} - E_{n\vec{k}})|\psi_{n\vec{k}}\rangle = 0$$, use Wannier expansion and dot with $\phi^*_m(\vec{r}-\vec{0})$:

$$\langle \phi_m(\vec{r}-\vec{0}) | (\mathcal{H} - E_{n\vec{k}}) \left(\frac{1}{\sqrt{N}} \sum_{\vec{R}} |\phi_n(\vec{r}-\vec{R})\rangle e^{i\vec{k}\cdot\vec{R}} \right) = 0$$

($\vec{r} \to \vec{R} = \vec{0}$)

$$\frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \left\{ \langle \phi_m(\vec{r}) | H | \phi_m(\vec{r}-\vec{R}) \rangle - E_{mk}\, \delta_{\vec{0},\vec{R}} \right\} = 0$$

$$\Rightarrow \boxed{E_{m\vec{k}} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \langle \phi_m(\vec{r}) | H | \phi_m(\vec{r}-\vec{R}) \rangle}$$

This expression is formally exact, but is not so useful because we do not know the Wannier states.

The tight-binding approximation assumes that each Wannier state can be approximated by a unperturbed atomic orbital,

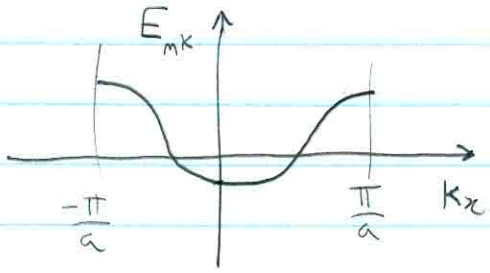
$$|\phi_m(\vec{r}-\vec{R})\rangle \approx |\Phi_m(\vec{r}-\vec{R})\rangle$$

and that only nearest neighbor matrix elements are appreciable. Hence

$$E_{m\vec{k}} \approx \underbrace{\langle \Phi_m(\vec{r}) | H | \Phi_m(\vec{r}) \rangle}_{E_{m0}} + \sum_{\substack{\vec{R}_{nearest} \\ neighbor}} e^{i\vec{k}\cdot\vec{R}_{nn}} \underbrace{\langle \Phi_m(\vec{r}) | H | \Phi_m(\vec{r}-\vec{R}_{nn}) \rangle}_{-V_m}$$

For a cubic lattice, $\vec{R}_{nn} = a\hat{x}, -a\hat{x}, a\hat{y}, -a\hat{y}, a\hat{z}, -a\hat{z}$:

$$E_{m\vec{k}} \approx E_{m0} - 2V_m \left[\cos(kx) + \cos(ky) + \cos(kz) \right]$$



- Tight binding approximation is good for bands arising from atomic orbitals with small overlap, $V_{2^{nd}\,n.n.} << V_{1^{st}\,n.n.}$.

Nearly free electron approximation

When atomic orbitals overlap significantly (opposite extreme of tight binding), the energy bands will be a small correction of the free electron energy $E_k = \frac{\hbar^2 k^2}{2m}$. To develop an approximation in this regime, consider the Bloch state

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}} c_n(\vec{k}-\vec{q}) e^{i(\vec{k}-\vec{q})\cdot\vec{r}}$$

Assume $c_n(\vec{k}-\vec{0}) \approx 1$ and $c_n(\vec{k}-\vec{q})$ for $\vec{q} \neq \vec{0}$ is much smaller than 1

Expand the crystal potential energy in a Fourier series:

$$U(\vec{r}) = \sum_{\vec{q}'} U(\vec{q}') e^{-i\vec{q}'\cdot\vec{r}} \qquad (\text{assume } U(\vec{q}=\vec{0}) = 0 \text{ (energy shift)})$$

Schrödinger eqn:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) - E_{n\vec{k}}\right]\psi_{n\vec{k}}(\vec{r}) = 0$$

$$= \frac{1}{\sqrt{V}} \sum_{\vec{q}} \left[\underbrace{+\frac{\hbar^2}{2m}(\vec{k}-\vec{q})^2}_{-\frac{\hbar^2}{2m}\nabla^2} + \sum_{\vec{q}'} U(\vec{q}') e^{-i\vec{q}'\cdot\vec{r}} - E_{n\vec{k}}\right] c_n(\vec{k}-\vec{q}) e^{i(\vec{k}-\vec{q})\cdot\vec{r}} = 0$$

Multiply by $\frac{1}{\sqrt{V}} e^{-i(\vec{k}-\vec{q}'')\cdot\vec{r}}$ and integrate over space:

$$\sum_{\vec{\varphi}} \left[+\frac{\hbar^2}{m}(\vec{k}-\vec{\varphi})^2 \delta_{\vec{\varphi},\vec{\varphi}''} + \sum_{\vec{\varphi}'} U(\vec{\varphi}') \delta_{\vec{\varphi}'',\vec{\varphi}+\vec{\varphi}'} - E_{mk}\delta_{\vec{\varphi},\vec{\varphi}''} \right] C_m(\vec{k}-\vec{\varphi}) = 0$$

$\vec{\varphi}'' = \vec{\varphi} + \vec{\varphi}'$

$$\boxed{\left[\frac{\hbar^2}{m}(\vec{k}-\vec{\varphi}'')^2 - E_{m\vec{k}}\right] C_m(\vec{k}-\vec{\varphi}'') + \sum_{\vec{\varphi}} U(\vec{\varphi}''-\vec{\varphi}) C_m(\vec{k}-\vec{\varphi}) = 0} \quad (*)$$

System of N equations (one for each $\vec{\varphi}''$) and N variables ($C_m(\vec{k}-\vec{\varphi}'')$).

Assume $E_{mk} \approx \frac{\hbar^2 k^2}{m}$ and keep only the $\vec{\varphi}=0$ term in the $\sum_{\vec{\varphi}} U_{\vec{\varphi}''-\vec{\varphi}}$:

$$\frac{\hbar^2}{m}\left[(\vec{k}-\vec{\varphi}'')^2 - k^2\right] C_m(\vec{k}-\vec{\varphi}'') + U(\vec{\varphi}'') \underbrace{C_m(\vec{k})}_{\approx 1} \approx 0$$

$$\Rightarrow \boxed{C_m(\vec{k}-\vec{\varphi}'') \approx \frac{-U(\vec{\varphi}'')}{\frac{\hbar^2}{m}\left[(\vec{k}-\vec{\varphi}'')^2 - k^2\right]}}$$

▶ we can insert this into $(*)$ with $\vec{\varphi}'' = \vec{0}$:

$$\left[\frac{\hbar^2}{m}k^2 - E_{m\vec{k}}\right] + \sum_{\vec{\varphi}} U(-\vec{\varphi}) \left[\frac{-U(\vec{\varphi})}{\frac{\hbar^2}{m}\left[(k-\vec{\varphi})^2 - k^2\right]}\right] \approx 0 \quad , \text{ use } U(-\vec{\varphi}) = U^*(\vec{\varphi}) \ (U(\vec{r}) \text{ is real})$$

$$\boxed{E_{m\vec{k}} \approx \frac{\hbar^2 k^2}{m} - \sum_{\vec{\varphi}} \frac{|U(\vec{\varphi})|^2}{\frac{\hbar^2}{m}\left[(\vec{k}-\vec{\varphi})^2 - k^2\right]}}$$

This is a good approximation provided the denominator does not blow up $\Rightarrow \vec{k}$ needs to be away from all $\frac{\vec{\varphi}}{2}$! ($\vec{k}$ away from BZ boundaries!)

When $\vec{k} = \frac{\vec{Q}_0}{2} - \Delta\vec{k}$ for some $\vec{Q}_0$ (and $|\Delta\vec{k}| << |\vec{Q}_0|$), $C_n(\vec{k}-\vec{Q}_0)$ can not be assumed small anymore; in this case we need to keep both $C_n(\vec{k})$ and $C_n(\vec{k}-\vec{Q}_0)$ and form a system of two equations:

$$\vec{Q}'' = 0 \Rightarrow \left[\frac{\hbar^2}{2m}k^2 - E_{n\vec{k}}\right] C_n(\vec{k}) + U(-\vec{Q}_0)\, C_n(\vec{k}-\vec{Q}_0) = 0$$

$$\vec{Q}'' = \vec{Q}_0 \Rightarrow \left[\frac{\hbar^2}{2m}(\vec{k}-\vec{Q}_0)^2 - E_{n\vec{k}}\right] C_n(\vec{k}-\vec{Q}_0) + U(\vec{Q}_0)\, C_n(\vec{k}) = 0$$

($\nearrow$ dropped $O(\Delta k)^2$)

$$\begin{pmatrix} \frac{\hbar^2}{2m}\left[\left(\frac{\vec{Q}_0}{2}\right)^2 - \vec{Q}_0\cdot\Delta\vec{k}\right] - E_{n\vec{k}} & U^*(\vec{Q}_0) \\ U(\vec{Q}_0) & \frac{\hbar^2}{2m}\left[\left(\frac{\vec{Q}_0}{2}\right)^2 + \vec{Q}_0\cdot\Delta\vec{k}\right] - E_{n\vec{k}} \end{pmatrix} \begin{pmatrix} C_n(\vec{k}) \\ C_n(\vec{k}-\vec{Q}_0) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\det(\;) = 0 \Rightarrow \left[\frac{\hbar^2}{2m}\left(\frac{\vec{Q}_0}{2}\right)^2 - E_{n\vec{k}}\right]^2 - \left(\frac{\hbar^2}{2m}\vec{Q}_0\cdot\Delta\vec{k}\right)^2 - |U(\vec{Q}_0)|^2 = 0$$

$$\left[E_{n\vec{k}} - \frac{\hbar^2}{2m}\left(\frac{\vec{Q}_0}{2}\right)^2\right]^2 = |U(\vec{Q}_0)|^2 + \left(\frac{\hbar^2}{2m}\vec{Q}_0\cdot\Delta\vec{k}\right)^2$$

$$\boxed{E_{n\vec{k}} = \frac{\hbar^2}{2m}\left(\frac{\vec{Q}_0}{2}\right)^2 \pm \sqrt{\left(\frac{\hbar^2}{2m}\vec{Q}_0\cdot\Delta\vec{k}\right)^2 + |U(\vec{Q}_0)|^2}}$$

A gap opens up at $\vec{k} = \frac{\vec{Q}_0}{2}$ (the BZ zone boundary); $\Delta_{Gap} = 2|U(\vec{Q}_0)|$.

→ Show slide comparing free electron theory to nearly-free theory. (at Crystal Structures Energy Bands)